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BENCHSCALE STUDIES OF LIMESTONE CALCINATION AND SULFATION - TGA HUMIDIFICATION STUDIES

Report No 88-202-K

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ABSTRACT

This report presents the results of a benchscale study of the effect of in-duct humidification of furnace-injected limestone-based sorbents on additional SO_2 removal. Four levels of relative humidity, 0, 27, 56 and 77% RH @ 70°C, and temperatures in the range of 80-1000°C were studied. Two high calcium limestones, Beachville and Pt. Anne, the dolomite King and Beachville hydrated lime were tested. At temperatures below about 350°C and above 600°C humidification was not found to improve the rate or extent of additional SO_2 capture by the partially sulfated sorbents. At temperatures between 400°C and 600°C, some improvement in SO_2 removal was observed with humidification. Our results suggest that the presence of liquid water is essential for enhancement of SO_2 removal by partially sulfated sorbents at the low temperatures encountered in the furnace duct.

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35-522-091	837.24	August 30, 1988	88-202-K

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EXECUTIVE SUMMARY

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A. Kalvins and B. Handy
Environmental Science Section
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This report presents the results of a benchscale study of the effect of in-duct humidification of furnace-injected limestone-based sorbents on additional SO_2 removal. Four levels of relative humidity, 0, 27, 56 and 77% RH @ 70°C, and temperatures in the range of 80-1000°C were studied. Two high calcium limestones, Beachville and Pt. Anne, the dolomitic limestone King and Beachville hydrated lime were tested. The partially sulfated sorbents were generated using the benchscale quartz flow-through reactor and exposed to a humidified synthetic flue gas stream in the Thermal Gravimetric Analyzer (TGA). At temperatures below about 350°C and above 600°C humidification was not found to improve the rate or extent of additional SO_2 capture by the partially sulfated sorbents. At temperatures between 400°C and 600°C, some improvement in SO_2 removal was observed with humidification. These results are in contrast to reports by others. However in previous work the humidity was generated by evaporation of a water spray in the furnace duct, while in this work, water was present only in the gas phase. Our results suggest that the presence of liquid water is essential for enhancement of SO_2 removal by partially sulfated sorbents at the low temperatures encountered in the furnace duct.

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To

To: DR. D. MILLS
Director of Research

BENCHSCALE STUDIES OF LIMESTONE CALCINATION AND SULFATION - TGA HUMIDIFICATION STUDIES

A. Kalvins and B. Handy

1.0 INTRODUCTION

This report presents the results of a study of the effect of in-duct humidification of furnace-injected limestone-based sorbents on additional SO_2 removal. The work was carried out in support of Ontario Hydro's pilot and fullscale studies of the furnace limestone injection process for SO_2 control. This paper is the fifth in a series related to benchscale studies of this process. /1,2,3,4/

Reports in the literature suggest that humidification of partially sulfated sorbents in the duct upstream of the electrostatic precipitator (ESP), or other particulate collection device, may significantly improve their ability to capture SO_2. Consol found that humidification, by evaporation of water sprays, resulted in approximately 15% additional SO_2 removal across the system. The temperature of the flue gas in the humidifier varied from 300°F (150°C) at the inlet to 150°F (65°C) at the exit. The humidifier was operated at a 25-30°F approach to the water dew point. With the addition of chemical additives to the water, SO_2 capture could be improved by another 10%./5/

Humidification also helps to improve the performance of the ESP which is affected by the dramatic increase in concentration of particles exiting the furnace and the increase in particle resistivity as a result of having lime, limestone and calcium sulfate in the flue gas./6/ Humidification lowers particle resistivity, enhances electrical energization and reduces the gas volume which increases the effective SCA (Specific Collecting Area) of the ESP.

This report presents the results of our study of the effect of various levels of humidification and temperature on SO_2 capture by a number of partially sulfated Southern Ontario limestones. The sorbents studied included two high calcium limestones, Beachville and Pt. Anne, the dolomitic limestone King and Beachville hydrated lime. The effect of the additive $CaCl_2.2H_2O$ was also briefly studied. The partially sulfated sorbents were

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generated using the quartz flowthrough benchscale reactor described in earlier work./4/ The sulfated materials were then transferred to the Thermal Gravimetric Analyzer (TGA) for study of the effect of humidification on additional SO_2 capture. Use of the TGA to study the calcination and sulfation of Southern Ontario limestones was reported earlier./3/

2.0 THEORY

The mechanism by which humidification results in an improvement in SO_2 capture by $CaO/CaCO_3$-based sorbents is not clear. It may be that reactivation of a partially-sulfated sorbent occurs as shown in equations (1)-(3).

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (<400^oC) \quad (1)$$
$$CaSO_4 + 1/2H_2O \longrightarrow CaSO_4.1/2H_2O \qquad (<163^oC) \quad (2)$$
$$CaSO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O \qquad (<128^oC) \quad (3)$$

Molecular volumes of the hydrated compounds are higher relative to the anhydrous species, therefore hydration causes the volume of the grains to increase. On subsequent dehydration, when treated sorbent is again exposed to hot temperatures, the reverse reactions occur and new pores are formed in the swelled structure, more or less in the same way as the formation of pores during calcination./7/ In the duct on route to the ESP or baghouse the sorbent is not however reheated. This mechanism applies more to reactivation, ie, when partially sulfated material is collected, humidified and recycled back into the furnace.

It is not clear what happens in the duct. At the low temperatures encountered in the duct, reaction of CaO with SO_2 is very slow. CaO will adsorb SO_2 in the 300-400^oC range and react with SO_2 to give $CaSO_3$ at temperatures above 400^oC./8/ At higher temperatures $CaSO_3$ decomposes to give $CaSO_4$, equation 4. At 1000^oC $CaSO_3$ is almost completely decomposed.

$$4\ CaSO_3 \longrightarrow 3\ CaSO_4 + CaS \qquad (>700^oC) \qquad (4)$$

The optimum temperature for reaction of CaO and SO_2 to form $CaSO_4$ is in the range 800-1000^oC./9/

Calcium hydroxide, $Ca(OH)_2$, reacts directly with both SO_2 and CO_2 at temperatures in the range of 400-650^oC, equations 5 and 6. Above 540^oC (1000^oF) a large percentage of the hydroxide is converted to both $CaCO_3$ and CaO, while below this temperature $Ca(OH)_2$ reacts without dehydrating./10/

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O \qquad (5)$$
$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (6)$$
$$Ca(OH)_2 \longrightarrow CaO + H_2O \qquad (7)$$

If SO_2 removal is observed at the low duct temperatures (<150^oC), then water must be catalyzing the reactions. In this work the

effect of humidification, without the presence of liquid water droplets, was studied.

3.0 EXPERIMENTAL

Four sorbents were studied, two high calcium limestones Beachville and Pt. Anne, a dolomitic limestone King, and Beachville hydrated lime. All sorbents are commercially available from Southern Ontario quarries. These sorbents were also used in the previously reported benchscale studies./1,2,3/ The sorbents together with their elemental analyses are listed in Table 1.

TABLE 1

LIMESTONE ELEMENTAL COMPOSITION (%)
(expressed as the oxide)

Sorbent	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3
Beachville	93.2	1.4	1.7		
Pt. Anne	80.0	1.6	11.0		
King	54.1	37.3	2.6	0.8	0.4
B'ville Hyd Lime	97.3*	0.8	1.5	0.2	0.2

*$Ca(OH)_2$

The effect of one additive, $CaCl_2.2H_2O$, was also studied. The $CaCl_2.2H_2O$ was of reagent grade and commercially available. The limestones were screened to -325 mesh. The limestone-$CaCl_2.2H_2O$ mixtures were prepared by stirring or shaking the two materials together prior to injection into the quartz flowthrough reactor.

The sorbents were calcined and sulfated in the two-furnace quartz flowthrough reactor described in earlier reports./1,2,4/ The reactor was operated at 1000°C. The sorbents were sulfated using dry synthetic flue gas. The composition of the gas was 1.5% SO_2, 3.5% O_2, 16% CO_2 and 79% N_2. The sulfated samples were collected and transferred to the Thermal Gravimetric Analyzer (TGA) where the materials were exposed to a humidified synthetic flue gas mixture. The composition of the gas was 1.3% SO_2, 3% O_2, 12.6% CO_2 and 65.9% N_2. The gas humidities studied varied from 0-77% RH, corrected to 70°C. These humidities resulted in a 29°C approach to the dew point at 27% RH, 13.9°C at 56% RH and 6.2°C at 77% RH. Care was taken to insure that the sorbent samples were never exposed to liquid water. This was done for two reasons, i) to insure that only the effect of water in the gas phase was studied and ii) to prevent/minimize corrosion of the instrument.

The principles of operation of a TGA were described in a previous report./3/ An attempt was made to simulate the conditions which the sorbent might experience when the sorbent-flue gas mixture is humidified in the duct upstream of the ESP. One parameter which could not however be simulated in the TGA was the short residence time the sorbent experiences in the duct. In the duct the residence time of the sorbent is on the order of seconds whereas in the TGA the average residence time was about 30 minutes. As in our previous work it was assumed that any trends observed in sorbent performance in the TGA would remain constant in the duct.

4.0 RESULTS AND DISCUSSION

The results are presented by limestone. After sulfation of the limestones in the flowthrough reactor the sulfur and calcium content of a fraction of the sample was analyzed using the wet chemical methods described in an earlier report/2/ and the remainder of the sample was used for the TGA studies. The results of the chemical analyses are presented in Table 2. Recall from earlier reports/1,2,3/, utilization is defined as the degree of sulfation of the available calcium. Humidity was deemed to cause additional sulfation if after a fixed period of time there was a measurable increase in the weight of the sample or a significant increase in the rate of weight gain relative to that which occurred under the same conditions but in the absence of humidification. An increase in sample weight may be due to sorbent hydration, (re)carbonation and/or sulfation. Attempts were made to identify the predominant reactions at each stage. Throughout the discussion of the results, ie, degree of sulfation versus temperature, the temperatures referred to are the final temperatures achieved during the run.

TABLE 2

SORBENT UTILIZATIONS OBTAINED USING THE BENCHSCALE FLOWTHROUGH REACTOR

Sorbent	Average Utilization (η)
Beachville	0.25
Pt. Anne	0.31
King	0.45
Beachville Hydrated Lime	0.23

4.1 Beachville

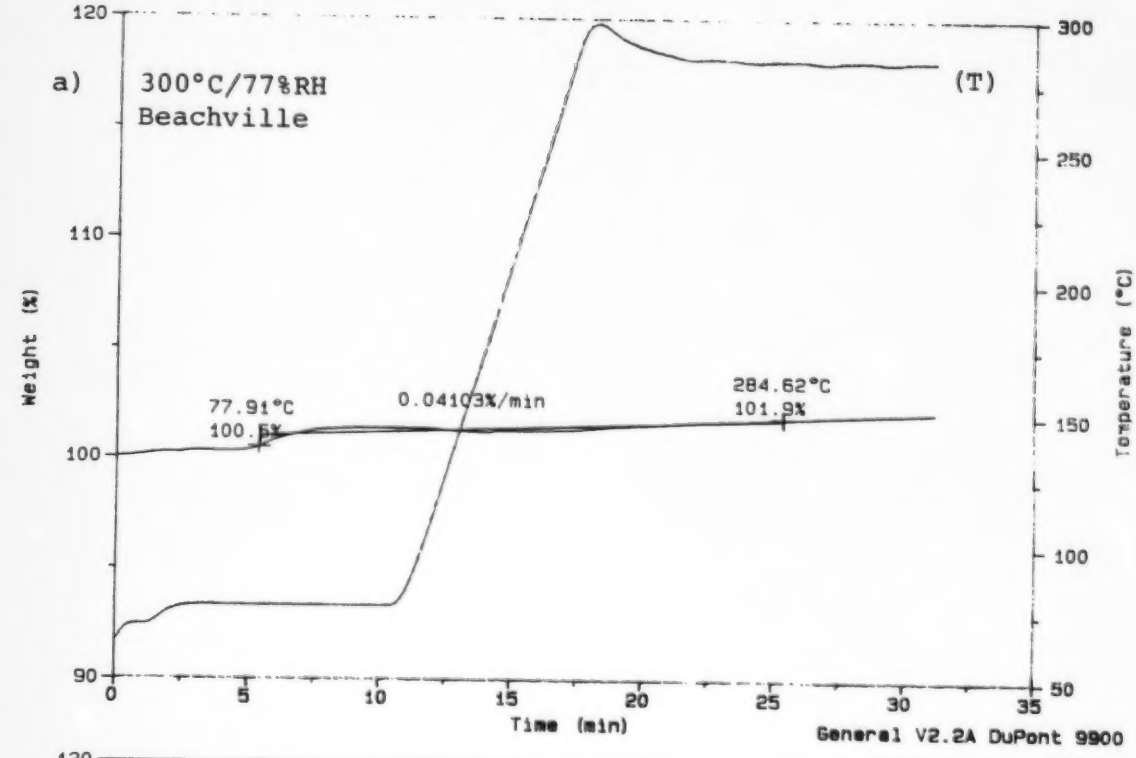
TGA sulfation studies of partially sulfated Beachville high calcium limestone were run at 80, 150, 300, 400, 500, 600 and 1000^{o}C and humidities ranging from 0 to 77% RH.

When reactor sulfated Beachville limestone was transferred to the TGA and exposed to the synthetic flue gas mixture in the temperature range 80-300°C and 77% RH, only a minimal increase in weight was observed, Figure 1a. When the samples were heated to temperatures above 300°C and under an atmosphere of high humidity there was a noticeable increase in sample weight. In the case of the 400°C/77% RH run, Figure 1b, as the temperature was ramped to 90°C a very gradual increase in weight was observed followed by a slight drop in weight. When the temperature reached 250-300°C, a rapid increase in weight was observed, 2.6%/min. These results suggest that hydration of the material occurs up to a temperature of about 90°C followed by dehydration at about 100°C and then sulfation, ie, a mechanism similar to that proposed by Schmal/7/ and described in Section 1.0.

When the sample was heated to 500°C (final temperature), under dry conditions, a rapid increase in weight, 2.2%/min, began about 370°C. Repeating the run under an atmosphere of 77% RH, a gradual increase in weight was observed as the system was heated to 85°C, 0.09%/min, followed by a slight drop in weight at about 100°C, probably due to hydration and dehydration. As the temperature approached 263°C, the weight of the sample increased rapidly, 3.3%/min. Similar results were obtained at 500°C and 56% RH, the sharp increase in weight, 2.0%/min, began at about 350°C.

The weight increase which began above 300°C in all of the runs may have been due to sulfation, recarbonation, or both. Heating a partially sulfated sample of Beachville to 500°C under 56% RH, in the absence of CO_2, resulted in a rapid increase in weight above 362°C, 2.5%/min. The run was repeated at 500°C/56%RH but without SO_2. An increase in weight of 1.18 %/min was observed starting at about 350°C. In both runs the rapid increase in sample weight began in the range 300-360°C. These results suggest competition between CO_2 and SO_2 for sites on CaO. Recarbonation of CaO, under dry conditions, is reported to begin about 290°C and become significant at about 400°C. In the presence of moisture, vapour or liquid H_2O, recarbonation occurs readily at atmospheric temperatures. H_2O appears to exert a catalytic effect./8/

When the system was heated to 600°C under 27% RH, again there was little change in the weight of the sample from about 20°C to 340°C. Above 340°C a rapid increase in SO_2 uptake, 2.7%/min, was observed. Under the same temperature and flue gas conditions, and 77% RH, a slow weight increase began at approximately 80°C, 0.2%/min, Figure 1c. Between 300 and 400°C, ie, about 350°C, the rate of weight pickup increased sharply, 2.7%/min. At 600°C and both of the humidities tested, 27 and 77% RH, the rate of weight increase was the same. This suggests that either a critical minimum humidity has been achieved, or at temperatures above 600°C, humidity has little effect on additional SO_2 uptake. At 77% RH the initial degree of weight increase, ie, below 100°C, was however greater than that at 27% RH.



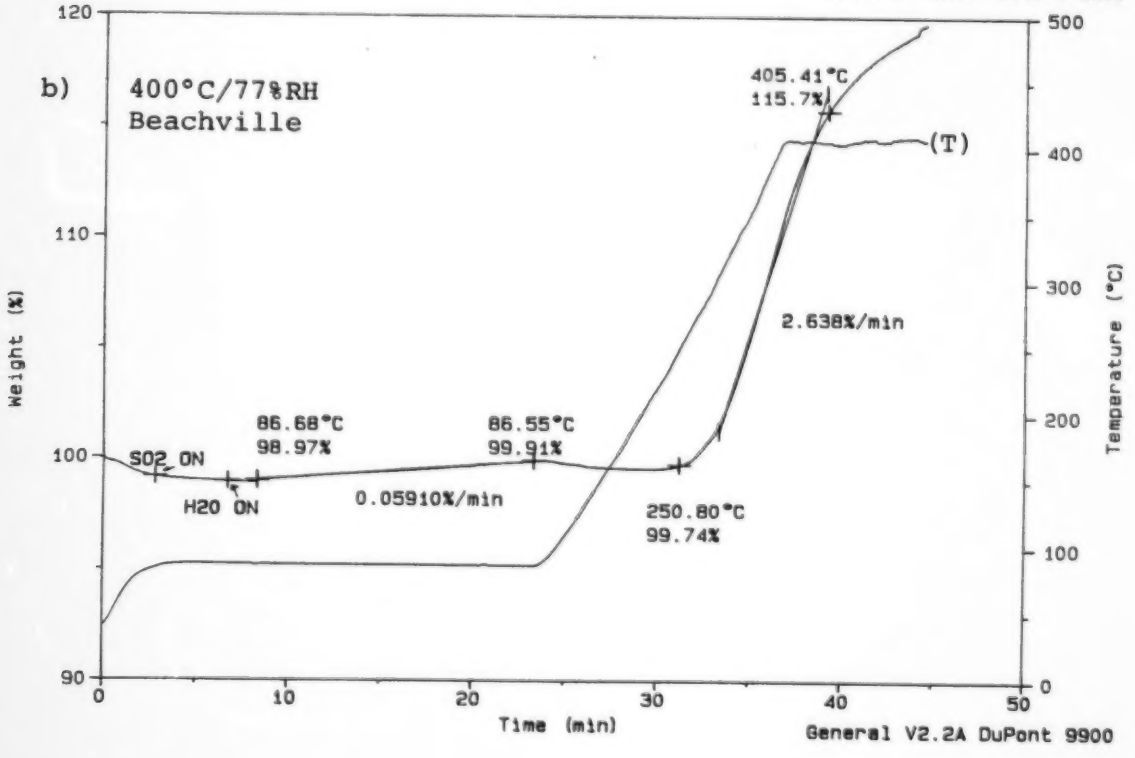


FIGURE 1a and b

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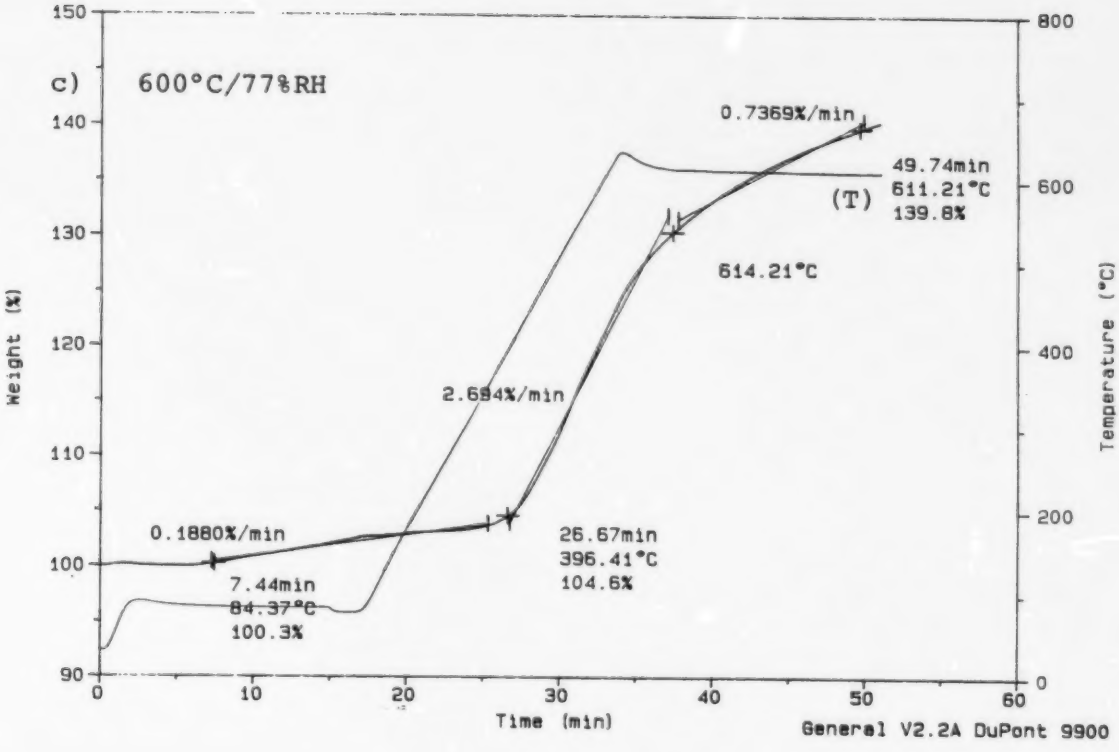

FIGURE 1c. TGA curves obtained when partially sulfated Beachville was exposed to the synthetic flue gas mixture under the following conditions: a) 300°C/77%RH, b) 400°C/77%RH, c) 600 °C/77%RH.

When the partially sulfated material was heated to 1000°C under 0 and 25% RH, there was no difference in the rate of additional SO_2 uptake between the two relative humidities. The results of the 1000°C/27% RH run are shown in Figure 2. As can be see from the graph, the weight change curve obtained at 1000°C/27% RH shows four segments. The weight increase beginning at about 400°C appears to be the result of both recarbonation and sulfation. At about 820°C there is a slight weight loss suggesting some calcination, followed by a further increase in weight as a result of sulfation. The run under dry conditions yielded a very similar curve. In both cases an increase in weight of about 40-44% was observed over a period of 20 minutes.

A summary of the results, % weight increase as a function of temperature and relative humidity, for the partially sulfated high calcium limestone Beachville is presented in the form of a bar graph in Figure 3. From the graph it is clear that at low temperatures, <300°C, humidification does not result in additional SO_2 uptake. Only at temperatures above 300°C does any significant weight increase occur. The cause of this weight increase is not clear. Recall that the optimum temperature for the formation of $CaSO_4$ is in the range 800-1000°C, and below 800°C the reaction is very slow. At temperatures about 400°C $CaSO_3$ is formed first and then oxidized. To check for the formation of $CaSO_3$, the sample would have to be chemically analysed, however the TGA runs do not generate sufficient material for this type of analysis. Above 500°C and at 1000°C, although there is a significant increase in weight, the level of humidification appears to have little impact on the rate or extent of the weight increase.

4.2 Pt. Anne

The effect of humidification on SO_2 capture by the partially sulfated high calcium limestone Pt. Anne was studied in detail over the temperature range 80-1000°C and 0-77% RH.

When the reactor calcined and sulfated material was exposed to 80°C and 56% RH for 30 minutes, essentially no weight increase was observed, 0.02%/min. Repeating the run at 77% RH, an approximate 1.4% weight increase was observed over a period of 20 minutes, 0.05%/min. This weight change is believed to be due to hydration.

When the runs were repeated at 200, 300 and 350°C, under 27% RH, no or only a minimal weight change, ie, 0.01%/min, was observed. Heating to 300°C under 77% RH resulted in a weight increase of approximately 0.07%/min.

When the partially sulfated sample was heated to 400°C, under dry conditions, a slight weight increase, 0.3%/min, was observed above 330°C. At 400°C/27% RH a weight increase of 0.8%/min was observed. To determine whether the increase in weight was due to sulfation or recarbonation the run was repeated without SO_2. At

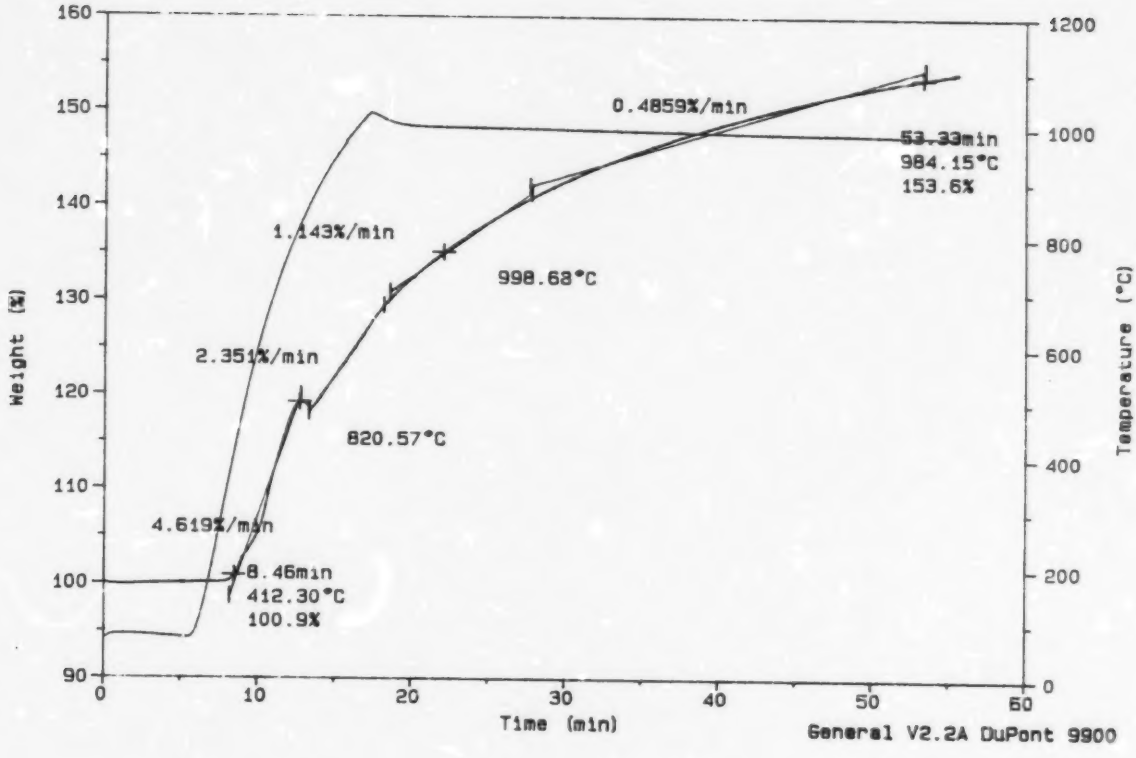

FIGURE 2. TGA curves obtained when partially sulfated Beachville limestone was exposed to the synthetic flue gas mixture, 27% RH, and heated to 1000°C.

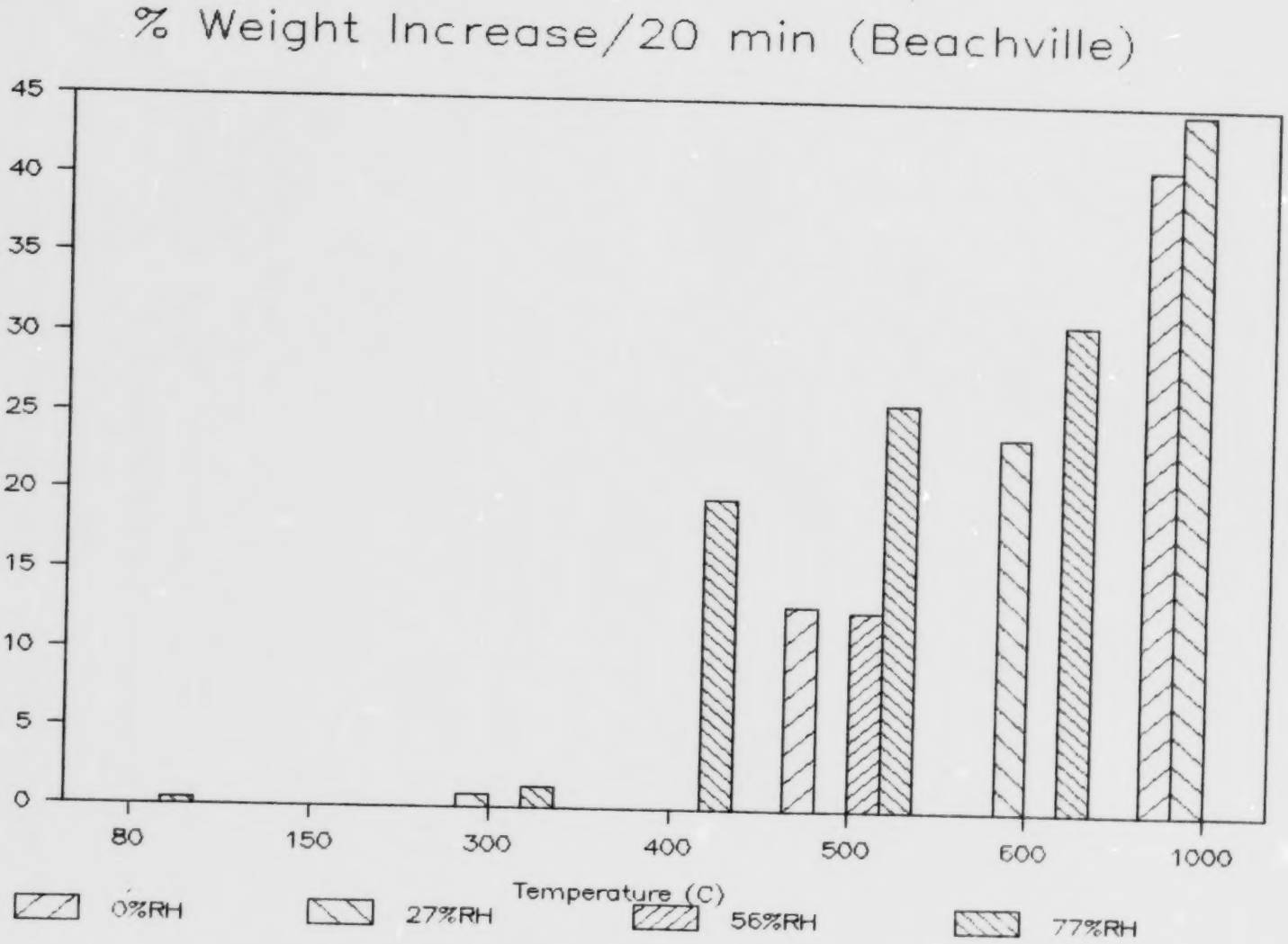

FIGURE 3. % Weight increase, after 20 min, as a function of temperature and relative humidity for the partially sulfated high calcium limestone Beachville.

27% RH, with no SO_2, a gradual weight increase was observed starting at about 340°C, 0.2%/min. Repeating the run, but without CO_2, a gradual increase in weight was observed starting at about 334°C, 0.4%/min. As in the case of Beachville, these results suggest competition between SO_2 and CO_2 for CaO. As the humidity was increased to 56% RH (400°C) the rate of weight increase, beginning at about 340°C, was 0.5%/min, and at 400°C/77% RH an increase of 0.9%/min was observed.

At 500°C, under dry conditions, exposure of the partially sulfated material to the synthetic flue gas resulted in a significant weight increase, see Figure 4a. The weight curve can be divided into 3 segments with the following slopes, 0.4, 1.0 and 0.4 %/min, resulting in an overall weight increase of 12% over a period of 25 minutes. At 500°C and 27% RH, Figure 4b, the weight curve can be divided into 4 segments with the following slopes, 0.8, 1.5, 0.5 and 0.2%/min, to give an overall weight increase of 12%/30 min. Under conditions of 500°C and 56% RH, a rapid increase in weight began above 350°C, 1.5%/min, Figure 4c. As the temperature approached 500°C the rate of increase slowed to 0.6%/min, resulting in an overall weight increase of 15% over a period of 15 minutes. These results suggest some enhancement in the rate of SO_2 uptake with humidification.

At 600°C, under dry conditions, the rapid weight increase begins about 347°C. Above this point the weight curve can be divided into 3 segments having slopes of 0.3, 1.8 and 0.2%/min, to give an overall weight increase of 11.3%/17 min. Under the same conditions, but 27% RH, the weight increase begins at 367°C. The curve appears to have 2 segments with the rates 3.2 and 0.2%/min. The overall weight change measured was approximately 16%/20 min. In this case there is a significant difference in the initial rate of weight change between the two curves obtained at 0 and 27% RH. In both cases, however, the rate of weight increase levels off at 600°C. At 56% RH the average rate of weight increase is approximately 1.2%/min or 13%/15 min. At 77% RH, again the curve is made up of 3 segments with the following slopes, 1.3, 2.5 and 0.8%/min, resulting in a total weight change of 34%/27 minutes. Again there appears to be a slight enhancement in SO_2 uptake with humidification (77% RH).

At 1000°C, there was no difference in the rate of weight change or overall weight increase between the runs done under dry conditions and 27% RH.

The results for the Pt. Anne limestone are summarized in the % weight increase as a function of temperature and relative humidity bar graph shown in Figure 5. As in the case of the Beachville limestone, below 300°C, exposure of partially sulfated Pt. Anne to SO_2 and humidity resulted in only a minimal weight increase. In the temperature range 300-600°C, humidification may have some impact on the rate of sulfation, but it does not appear to be as great as that suggested by others./5/ Above 600°C, a significant increase in weight was observed, but except in the

Pt. Anne

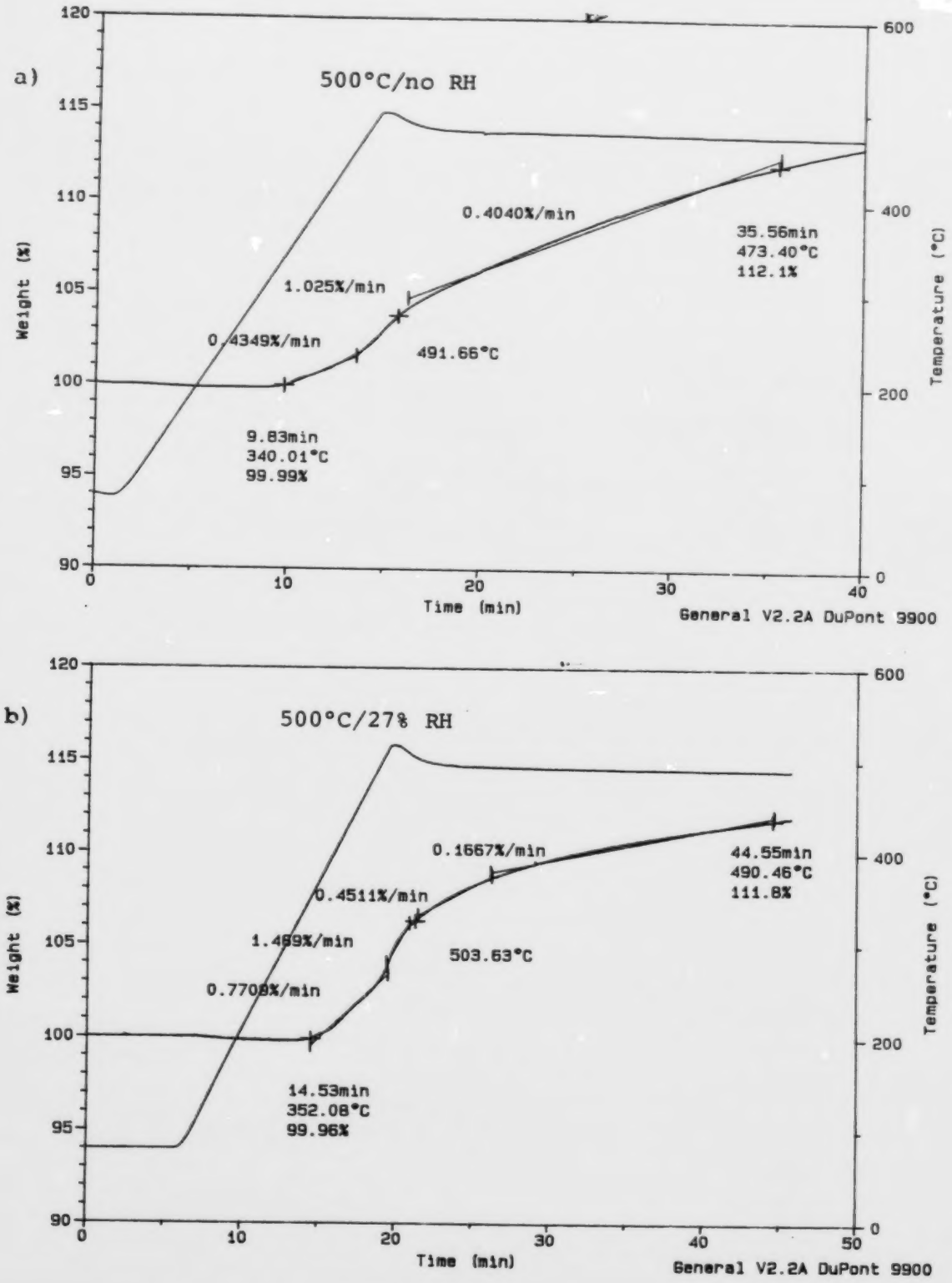

FIGURE 4a and b

c)

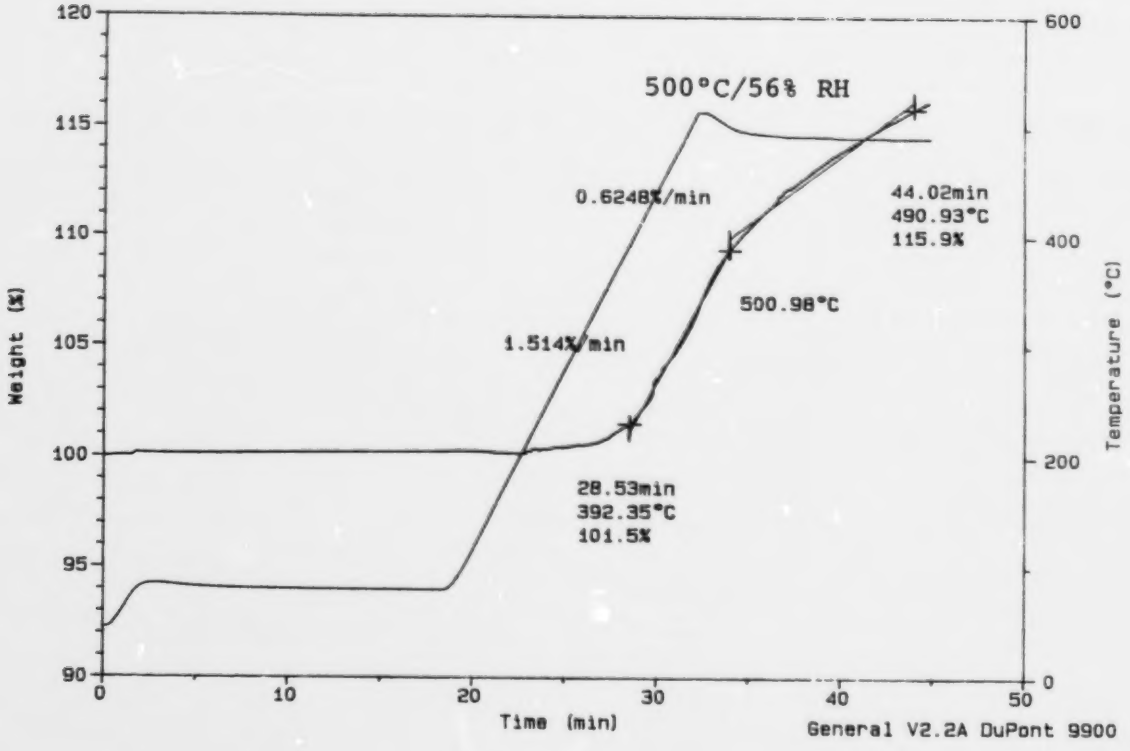

FIGURE 4c. TGA curves obtained when the partially sulfated Pt. Anne limestone was exposed to the synthetic flue gas mixture under the following conditions:

a) 500°C / no RH
b) 500°C / 27% RH
c) 500°C / 56% RH

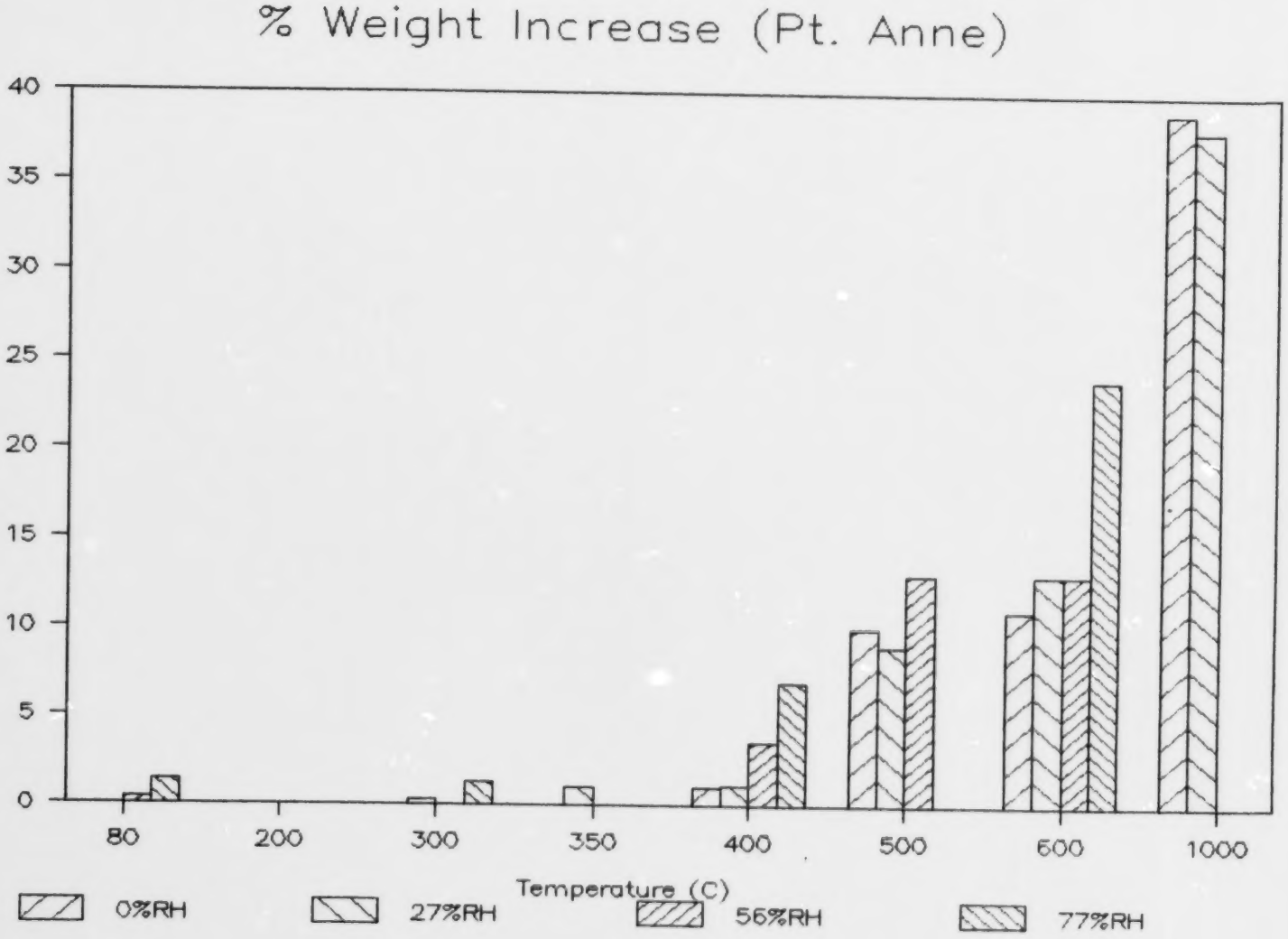

FIGURE 5. % Weight increase, after 20 minutes, as a function of temperature and % relative humidity for the partially sulfated high calcium limestone Pt. Anne.

case of very high humidity, 77% RH, the rate and extent of the increase was independent of the level of humidification.

4.3 King

The effect of humidification on SO_2 capture by the partially sulfated dolomite King was studied at temperatures of 80, 150, 300, 400, 500, 600 and 1000°C and relative humidities of 0-77%.

When the sample was heated at 56% RH and 80°C a gradual increase in weight was observed, 0.2%/min. As the temperature was ramped to 150°C, no further change in weight was observed, ie, no increase or decrease. The run was repeated at 56% RH. After heating the sample at 80°C for 15 minutes the temperature was ramped to 300°C. While the sample was heated at 80°C there was a gradual increase in weight, 0.1%/min. When the temperature reached 100°C the weight of the sample dropped suddenly, 1.4%/min, resulting in no net weight gain. No further change in weight was observed as the temperature climbed to 300°C. Similar results were obtained at 300°C/77% RH. All of these results suggest that at low temperatures, <300°C, any weight gain is due primarily to hydration of the sample.

When the sample was heated to 400 and 500°C under 56% RH, a similar pattern in weight change was observed, ie, slow weight increase to approximately 100°C followed by a rapid drop in weight. In both cases however, when the temperature of the sample reached 340-360°C a rapid increase in weight was observed. At 400°C an overall weight increase of 10%/15 min was observed, and at 500°C, an overall weight increase of 17%/12 min was recorded.

Similarly at 600°C and 27, 56 and 77% RH, a significant weight increase began between 310-340°C resulting in an average weight gain of 32-38% over a period of about 20 min. No significant difference was observed in the degree or rate of weight change as a function of the level of humidification. Again it appears that a minimum temperature of approximately 320-340°C is required in order for a significant additional rate of sulfation to occur and humidification has little impact on the rate or extent of the weight change.

The results are summarized in the form of a bar graph in Figure 6.

4.4 Beachville Hydrated Lime

The effect of humidification on additional sulfation by partially sulfated Beachville hydrated lime was studied at temperatures of 80, 300, 400, 600 and 1000°C and relative humidities of 0, 27, 56 and 77%.

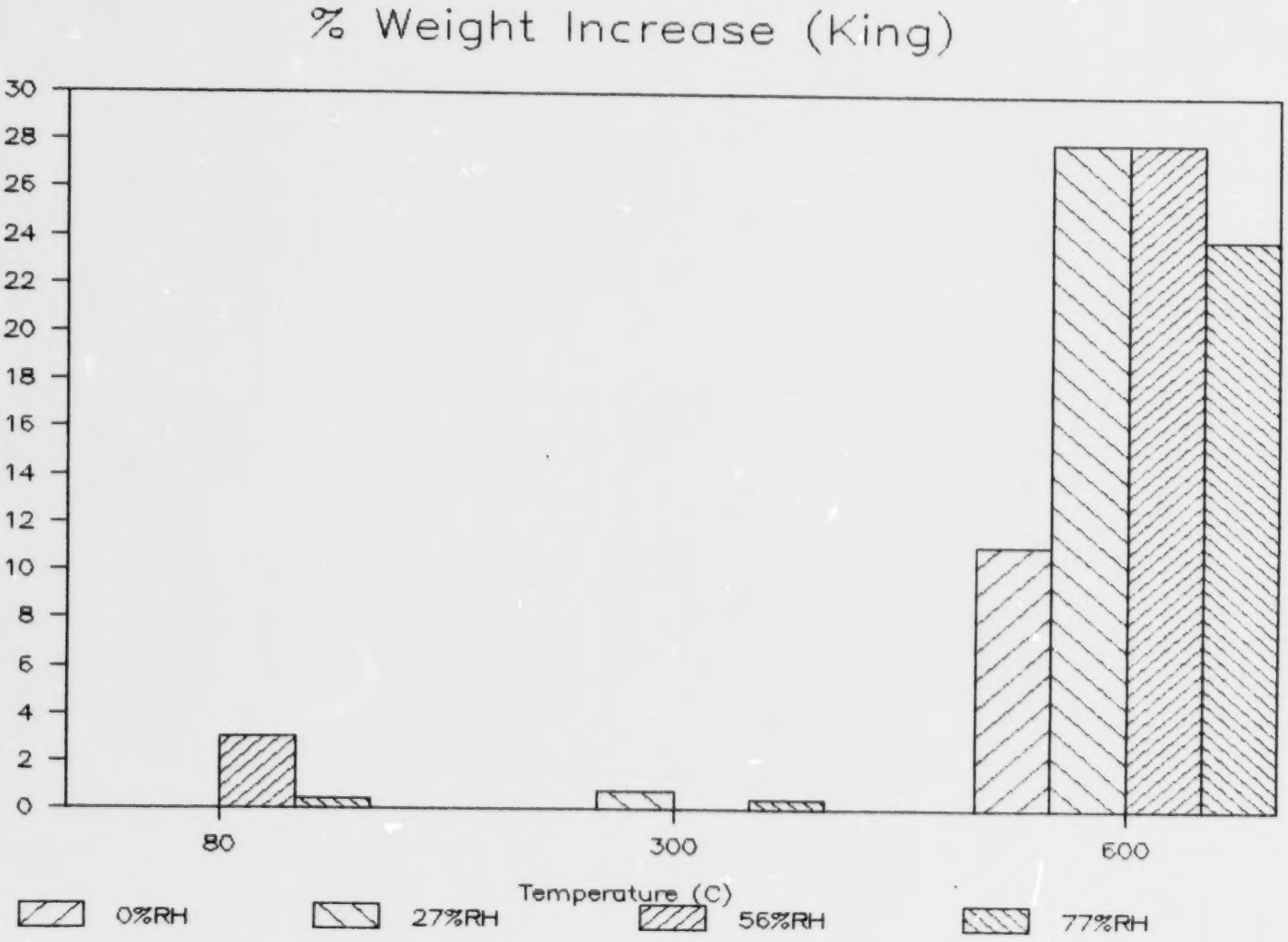

FIGURE 6. % Weight increase, after 20 minutes, as a function of temperature and % relative humidity for the partially sulfated dolomitic limestone King.

Heating the partially sulfated material to 80°C under 56% RH resulted in a gradual weight increase, 0.05%/min. Under conditions of 77% RH, a more rapid increase in weight, 0.31%/min, was observed. Slow increases in weight were also observed when the runs were repeated in the absence of humidity and in the absence of SO_2. These results suggest that the weight gain by the sample is due to both reaction with SO_2 and hydration.

Under conditions of 300°C and 56% RH, heating the sample from 80 to 100°C resulted in only a very slight increase in weight. As the temperature rose to 166°C a gradual increase in weight, 0.16%/min, was observed. Under conditions of 300°C and 77% RH, a rapid increase in weight, 1.05%/min, began at about 250-290°C. When the run was repeated without humidification, a gradual weight increase, 0.4%/min, began at about 240°C.

Under conditions of 400°C/56% RH, the sample weight began to increase at about 344°C, 0.96%/min. Similarly at 77% RH a slow increase in weight began at about 80°C followed by a faster rate of weight gain, 1.07%/min, beginning at 343°C.

Under conditions of 600°C and 56% RH a very slow weight increase began at about 194°C, followed by a rapid increase in weight when the system reached 370°C, resulting in a total weight change of 27%/28 min.

The experiment was also run at 1000°C and the times at which H_2O and SO_2 were added to the system were staggered. The results are shown in Figure 7. The sample was heated from approximately 80 to 900°C under an atmosphere containing 65.9% N_2, 3% O_2, 12.6% CO_2, no SO_2 and 27% RH. A rapid increase in weight, 5.3%/min, began at about 427°C; once the temperature reached 695°C, the weight of the sample dropped rapidly, -9.5%/min. These results suggest some initial sorbent recarbonation followed by calcination. With the addition of SO_2 to the flue gas at about 900°C, a rapid increase in weight, 4.3%/min, was observed resulting in an overall weight increase of 42.4%/11 min.

The results collected for Beachville hydrated lime are summarized in bar graph form in Figure 8. As with the other partially sulfated materials, a significant increase in weight began above 400°C. However, in contrast to the results obtained with the other limestones, at low temperatures (<400°C) a greater increase in weight was observed with the hydrated lime. At 80°C this weight increase is however believed to be primarily due to hydration, not sulfation.

4.5 Effect of the Additive $CaCl_2.2H_2O$

The effect of the additive $CaCl_2.2H_2O$ and humidification on additional SO_2 uptake by the high calcium limestone Pt. Anne and the dolomite King was also studied.

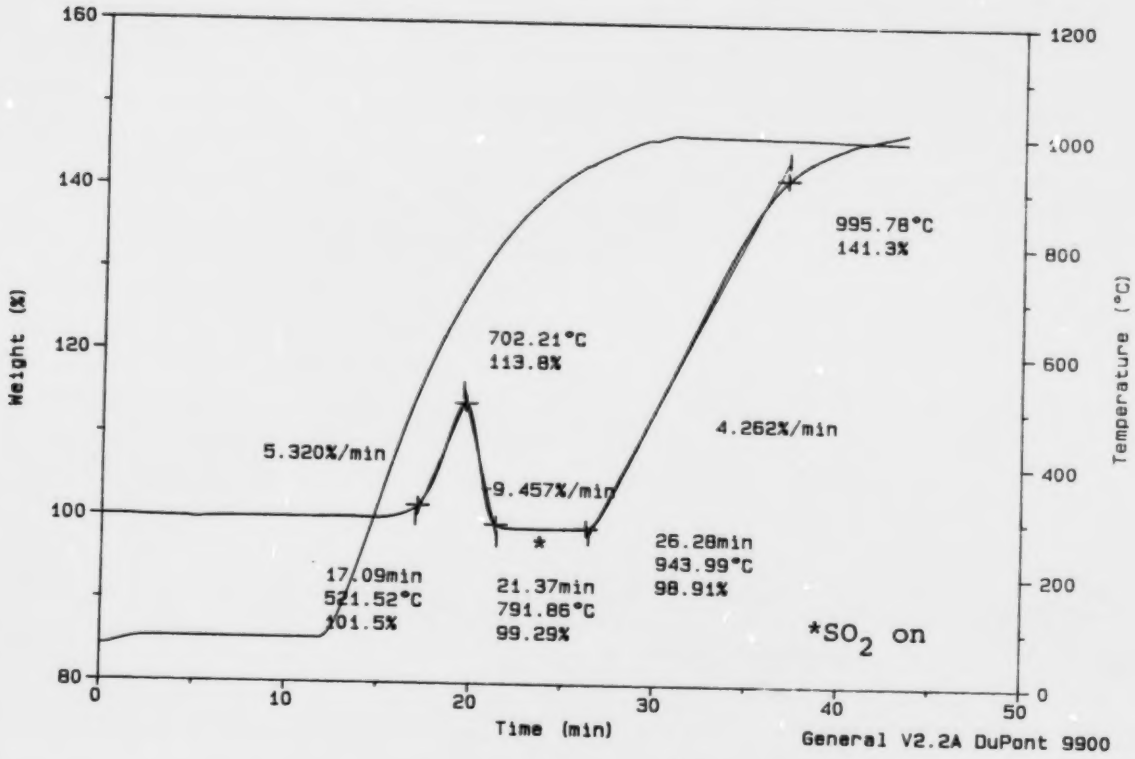

FIGURE 7. TGA curve obtained when partially sulfated Beachville hydrated lime was exposed to the synthetic flue gas mixture, 27% RH and heated to 1000°C. * indicates the point at which 1.3% SO_2 was added to the flue gas mixture.

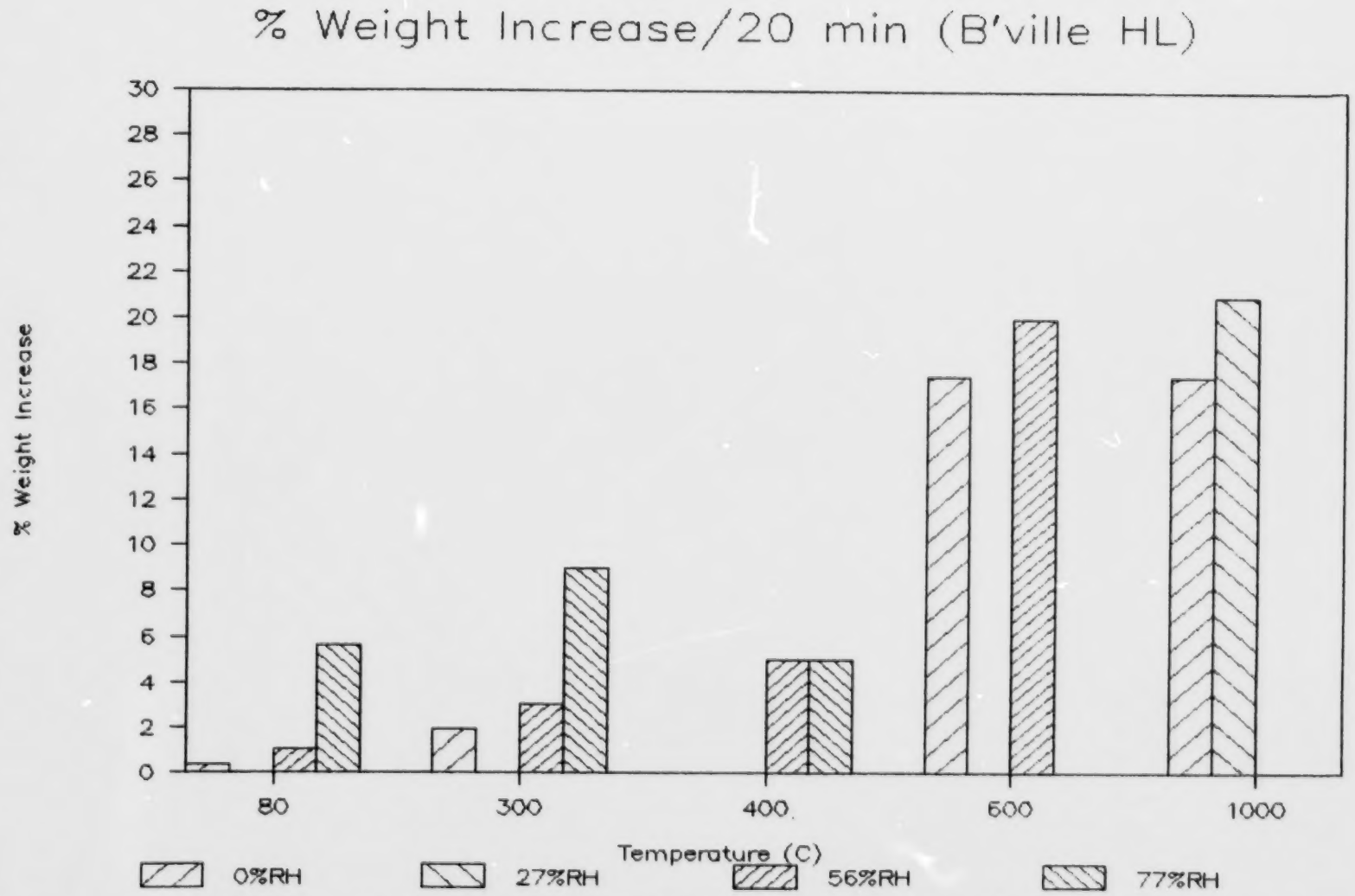

FIGURE 8. % Weight increase, after 20 min, as a function of temperature and % relative humidity for partially sulfated Beachville Hydrated Lime.

4.51 Pt. Anne

When partially sulfated Pt. Anne mixed with 1% $CaCl_2.2H_2O$ was heated to 150°C under a synthetic flue gas mixture and 56% RH, no additional SO_2 uptake was observed. Similarly at 300°C and 77% RH no additional SO_2 uptake was observed.

The run was repeated at 56% RH and 500°C, however the sample was "conditioned" for approximately 15 min under an atmosphere of 1.3% SO_2 and 56% RH at 80°C and then the temperature was ramped to 500°C. Above 400°C a noticeable increase in weight began, 0.7%/min, to give a total weight increase of 9%/12 min. Comparison of these results with those obtained under identical conditions but without $CaCl_2.2H_2O$, 14.4%/15.5 min, suggests no real improvement in SO_2 pick-up in the presence of $CaCl_2.2H_2O$.

When the run was repeated at 600°C and 77% RH, a rapid increase in weight began at about 385°C, resulting in an overall weight increase of 36.8%/16 min. In the absence of $CaCl_2.2H_2O$ an overall weight increase of 34% was observed only after 27 min.

Similarly at 56% RH and 600°C, in the presence of $CaCl_2.2H_2O$ an overall weight increase of 21%/7 min was recorded in contrast to 13% over 15 min without the additive.

From these results it can be concluded that at 600°C and high humidities, 56 and 77%RH, $CaCl_2.2H_2O$ may cause some enhancement in SO_2 removal.

4.52 King

When a partially sulfated mixture of King and 1% $CaCl_2.2H_2O$ was exposed to 56% RH (no SO_2) and heated to 80°C, a slow increase in weight was observed, approximately 0.3%/min for the first 10 min followed by 1%/min for the next 20 min. When 1.3% SO_2 was added to the system a rapid increase in weight was observed, 1.2%/min for 5 min, followed by a levelling off in rate to 0.2%/min. Under identical conditions, without $CaCl_2.2H_2O$, the rate of weight increase was about 0.1%/min.

In contrast to the previous results, when the system was equilibrated at 80°C and 56% RH in the presence of SO_2 a rapid increase in weight, 2.4 %/min, was observed. As the temperature of the sample was increased to 300°C, the weight of the sample began to drop, 1.0 %/min, Figure 9. The rate of weight loss however levelled off at about 280°C. The overall increase in weight was approximately 7%. Without $CaCl_2.2H_2O$ a similar pattern of events was also observed, however there was no overall weight gain. Similarly when the system was heated to 400°C under 56% RH, as the temperature rose to 80°C there was a slow increase in weight, 0.4%/min. Between 80 and 340°C the weight of the sample dropped and at 340°C, a rapid increase in weight, 1.3%/min, was observed. The overall increase in weight was

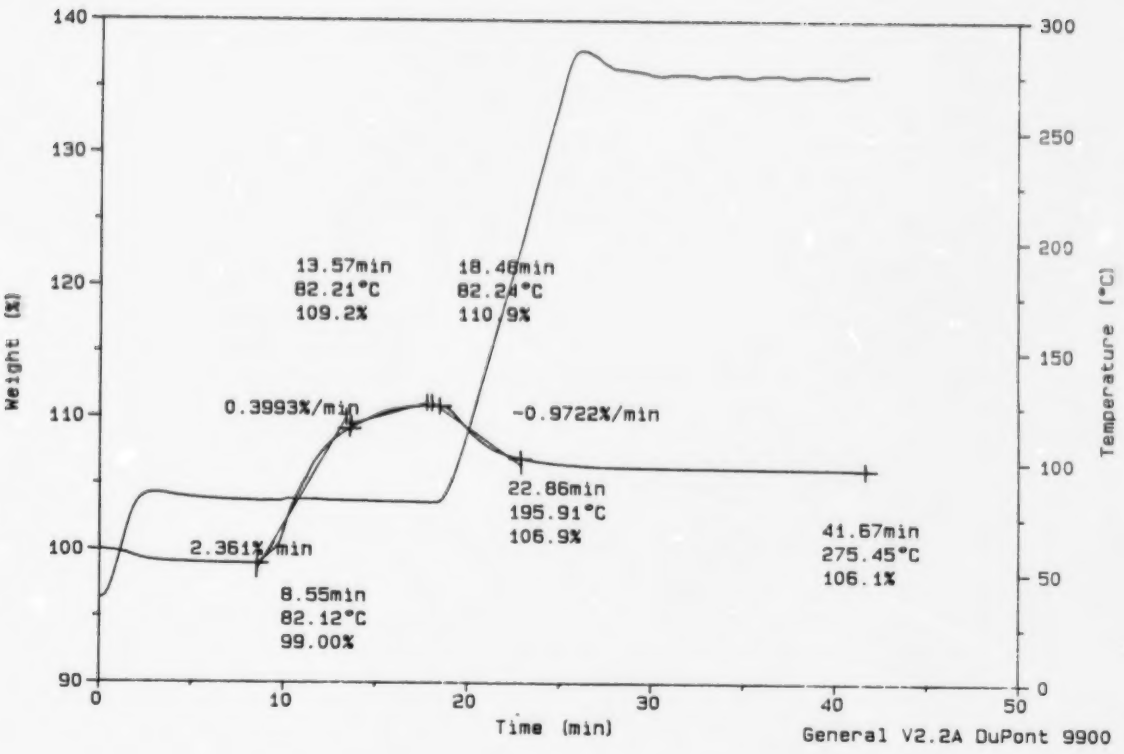

FIGURE 9. TGA curve obtained when a mixture of the partially sulfated dolomite King and 1% $CaCl_2.2H_2O$ (W/W) was exposed to the synthetic flue gas mixture, 56% RH and heated to 300°C.

approximately 10%/18 min. Without the additive, under identical conditions, the total weight change was 10%/15 min.

Similar results were also obtained at 600°C/56% RH, ie, an initial weight increase and decrease followed by a weight increase due to sulfation (1.8%/min) beginning at about 400°C. The overall increase in weight was 22.5%/18 min, again lower than the rate observed in the absence of $CaCl_2.2H_2O$.

From these results it can be concluded that a minimum temperature of 300-350°C is required before sulfation occurs and in the case of a dolomite, the presence $CaCl_2.2H_2O$ does not enhance SO_2 uptake.

5.0 CONCLUSIONS

The effect of humidification of four partially sulfated calcium based sorbents on additional SO_2 uptake was studied. At temperatures below about 350°C and above 600°C, humidification was not found to improve the rate or extent of additional SO_2 capture by the partially sulfated sorbents. At temperatures between 400 and 600°C, some improvement in SO_2 removal was observed with humidification. When 1% $CaCl_2.2H_2O$ was mixed with a high calcium limestone, some enhancement in SO_2 pickup was observed at high temperature (600°C) and high relative humidities (56 and 77% RH). No improvement in SO_2 pickup was observed in the case of the dolomite/$CaCl_2.2H_2O$ mixture.

The differences between the results obtained in this study and the results of others suggest that the presence of liquid water is essential to efficient SO_2 removal at low temperatures (<300°C). Recall that in the work reported by Consol the humidity in the duct was generated by evaporation of a water spray, ie, water was present in the liquid form at least initially. In contrast to these conditions, in the work described in this report, the water was always present as a gas.

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